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BROAD-BASED SEARCH FOR NEW AND PRACTICAL SUPERCONDUCTORS

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Final Report

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14. ABSTRACT: Over 300 new compounds were synthesized and characterized during this five year grant. Many new superconductors were discovered, most with transition temperatures (Tc) below 10K. One noteworthy discovery was the superconductivity found in $Ca_{1-x}La_xFe_2As_2$ at ~48K, the highest known transition temperature in this class of materials. New techniques, such as sulfur flux growth and combinatorial thin film growth, were developed that will aid in the search for higher Tc and more practical superconductors in the future. Collaboration with the Smithsonian Museum was established to search for superconductivity in their collection of over 300,000 minerals. To date, about 50 compounds have been measured with one superconductor (Tc ~4K) found at high pressure. Superconductivity was found to be enhanced in a nanocrystalline composite of a known low-Tc superconductor (Sn) and a high dielectric constant insulator (STO or BTO). This is a promising new approach for the future search for higher Tc superconductors. Over 64 papers were published on the research supported by this award and many invited talks (~90) were given by the PI and others supported by this award.

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2014 Final Report—Broad-based Search for New and Practical Superconductors (AFOSR-MURI #FA9550-09-1-0603)

R. L. Greene, University of Maryland, College Park

Overview

This report covers the fifth year of research done by the University of Maryland/UC San Diego/Iowa State University MURI project (1 Aug 2013 – 31 July 2014) as well as a brief overall summary of the major accomplishments of this 5-year MURI project. Between the three institutions we have carried out many hundreds of synthetic attempts to find new superconductors (a complete list of these is available upon request). A small percentage of these were successful (see below) and both the successes and failures have given us insight into where to search for superconductivity in the future. Most of the newly discovered superconductors have a transition temperature (Tc) below 10K, but, in our future research under another award, we plan to look at modifications of these materials and put them under high pressure in the hopes of finding higher Tc systems. We have also coordinated our efforts by exchange of samples and personnel, by Skype conference calls and by several annual meetings, where all participants in the MURI program give presentations on their research followed by an extensive discussion.

Five-year Major Research Accomplishments (see prior annual reports for details)

1) At UMD, superconductivity in the 45-50K range was discovered in rare-earth(R) doped $Ca_{1-x}R_xFe_2As_2$ crystals. This is the highest Tc found for these "122" compounds. Work is continuing to understand this higher Tc and how to possibly increase it.

2) At UMD, collaboration with the Smithsonian Museum was established to search for superconductivity in their collection of over 300,000 minerals. To date, about 50 compounds have been measured at UMD with one superconductor (Tc ~4K) found at very high pressure. With the acquisition of DURIP-supported equipment we will be able to carry out more rapid screening for superconductivity during the next few years.

3) At ISU, S-based fluxes were developed to enable the growth of S-based mineral compounds, which will be doped and/or put under pressure to see if superconductivity can be induced. There now is an active collaboration between ISU and UMD in the search for superconductivity in mineral compounds.

4) At UCSD, superconductivity was discovered below 10K in new layered LnO0.5F0.5BiS2 compounds, where Ln=La, Ce, Pr, Nd.

5) At UMD, combinatorial thin film spread methods were developed to search for new superconductors. A new polycrystalline Fe-B material was found with a Tc around 5K. More work is needed to fully characterize this Fe-B material and to expand this "combi" technique to other potential superconducting systems.

Past year research

The most significant research done during the past year is summarized here. A list of 2013-14 invited talks is also given. The complete list of all publications from the 5-years of MURI support is provided in a separate file, which includes those from the past year.

1. Superconducting Metamaterials

A recent proposal (arXiv:1311.3277) that the metamaterial approach to dielectric response engineering may increase the critical temperature of a composite superconductor-dielectric metamaterial has been tested in experiments with compressed mixtures of tin and barium titanate (BTO) and strontium titanate(STO) nanoparticles of varying composition. An increase of the critical temperature of the order of 0.15 K(~5%) compared to bulk tin has been observed for 40% volume fraction of BTO and STO nanoparticles. No increase in Tc was observed for diamond/tin mixtures, which suggests that the larger dielectric constant of STO and BTO was playing a role in the enhanced Tc. Although this Tc increase is small it does suggest that this approach to finding higher Tc superconductors is worthy of further exploration. ***This work is submitted to Nature materials (see arXiv:1408.0704).***

2. Iron-based Superconducting Materials

Pressure Synthesis of High Rare Earth Content $Ca_{1-x}R_xFe_2As_2$: A joint project in collaboration with the group of P. Canfield at Iowa State University focused on exploring the consequences of high percentage rare earth substitution (>25%) effects on the high-Tc superconducting state of this system. The project involved sending a graduate student (T. Drye) to ISU to assist in performing high-pressure synthesis of crystals under 6 GPa pressures and 1500C temperatures. This enabled us to synthesize crystals of $Ca_{1-x}R_xFe_2As_2$ with R=Pr, La concentrations up to 40%, greatly exceeding that possible using conventional ambient pressure growth techniques and allowing us to extend the anomalous phase diagram of the rare earth-doped system to help in understanding the nature of the superconducting phase in the heavily overdoped regime. ***This work is under preparation for submission.***

Separation of Antiferromagnetism and High-Temperature Superconductivity in $Ca_{1-x}R_xFe_2As_2$ Under Pressure: High pressure experiments completed in collaboration with G. Luke at McMaster University, Canada, M. Sutherland at University of Cambridge, UK, and J. W. Lynn at NIST-NCNR, study the effect of both quasi-hydrostatic and hydrostatic pressures on single crystals of $Ca_{1-x}La_xFe_2As_2$ with varying levels of La concentration in order to study the interplay of antiferromagnetic (AFM) and superconducting phases. Our results indicate that the AFM and structural transitions are gradually suppressed in underdoped crystals until superconductivity abruptly appears, indicating that this high Tc superconductivity is intrinsic and does not appear to coexist with AFM, much like the 1111 iron-oxypnictide superconductors. The unusual dichotomy between lower-Tc systems that happily coexist with AFM and tendency for the highest-Tc systems to show phase separation provides an important clue to the pairing mechanism in iron-based superconductors. ***This work is published in Phys. Rev. B 89, 134516 (2014).***

3. New/Unexplored Directions:

Search for Superconductivity in Naturally Occurring Mineral Compounds: In a new collaboration with curators C.M. Santelli and J.E. Post of the Smithsonian Institution's Museum of Natural History, we have gained access to the extensive collection of over 350,000 minerals maintained by the Department of Mineral Sciences for use in searching for superconducting phases. Preliminary studies have involved selection of compounds of interest together with the curators and Smithsonian collection manager, and systematic magnetic susceptibility scans as a function of temperature and magnetic field. To date, approximately 30 compounds have been scanned, resulting in the discovery of several previously unobserved magnetic transitions at low temperatures. With the future acquisition of DURIP-supported equipment to enable higher throughput screening of samples, we will be able to continue such work at a much higher rate of coverage. In conjunction, we have performed high-pressure transport and crystallography experiments in collaboration with J. Jeffries at LLNL on the mineral compound Sperrylite (PtAs2), revealing a superconducting transition near ~4 K at pressures exceeding 100 GPa. This work has motivated the search for similar compounds (eg. Krutovite, NiAs2) with similar effective unit cell as Sperrylite under pressure. Ongoing work is exploring chemical and pressure approaches to this, as well as searches of the SI mineral collection for related compounds. ***This work was recently highlighted in a news feature in Physics Today.***

4. Superconductivity in layered lanthanide oxygen bismuth sulfide compounds

Measurements of $\rho(T)$ between 1 K and 300 K at various pressures up to ~3 GPa were performed on the superconducting compounds $LnO_{0.5}F_{0.5}BiS_2$ (Ln = La, Ce, Pr, Nd). For each compound, a pressure-induced transition from a low T_c to a high T_c phase was observed. This transition correlates with a suppression of the semiconducting behavior with pressure to metallic, or nearly metallic, behavior. This research is reported in two recent manuscripts. On the other hand, to investigate the chemical pressure effect on the $LaO_{0.5}F_{0.5}BiS_2$ compound, the chemical pressure introduced by partial chemical substitution of lanthanum with smaller yttrium ions in

$La_{1-x}Yb_xO_{0.5}F_{0.5}BiS_2$ reduces the lattice parameter a and the unit cell volume V. It also reduces the volume fractions in the superconducting states of our samples. A plateau-like behavior is observed for the concentration-dependence of the superconducting critical temperature $T_c(x)$; although, a slight decrease of T_c is observed at low x. This behavior of $T_c(x)$ is probably caused by changes of the La–O–La bond angles with increasing x. Such a scenario suggests that the lattice parameter c plays an important role in determining T_c in this system. The plateau-like behavior of $T_c(x)$ indicates that chemical pressure is insufficient to induce either the high-T_c superconducting phase or the structural phase transition that is observed in $LaO_{0.5}F_{0.5}BiS_2$ under externally applied pressure.

5. Combinatorial investigation of superconductors

This year we continued making combinatorial libraries of systems which are potentially superconductors. In particular, we are exploring BaSnO3 as the base system to look for new superconductors. Doped BaSnO3 is a transparent conductor, and by controlling the doping and using ionic liquid gating, we hope to push its carrier density beyond $10^{21}/cm^3$ and beyond. This is the typical carrier density range for other oxide superconductors such as cuprates. So far we have fabricated and measured a variety of doped (A-site and B-site) BaSnO3 composition spreads. Figure 1 is a summary of one spread where we made a continuous spread of (Ba,La)SnO3. X-ray (left bottom) shows that we have continuous change in lattice constant across the spread which indicates that we are able to carry out continuous substitution into BaSnO3.

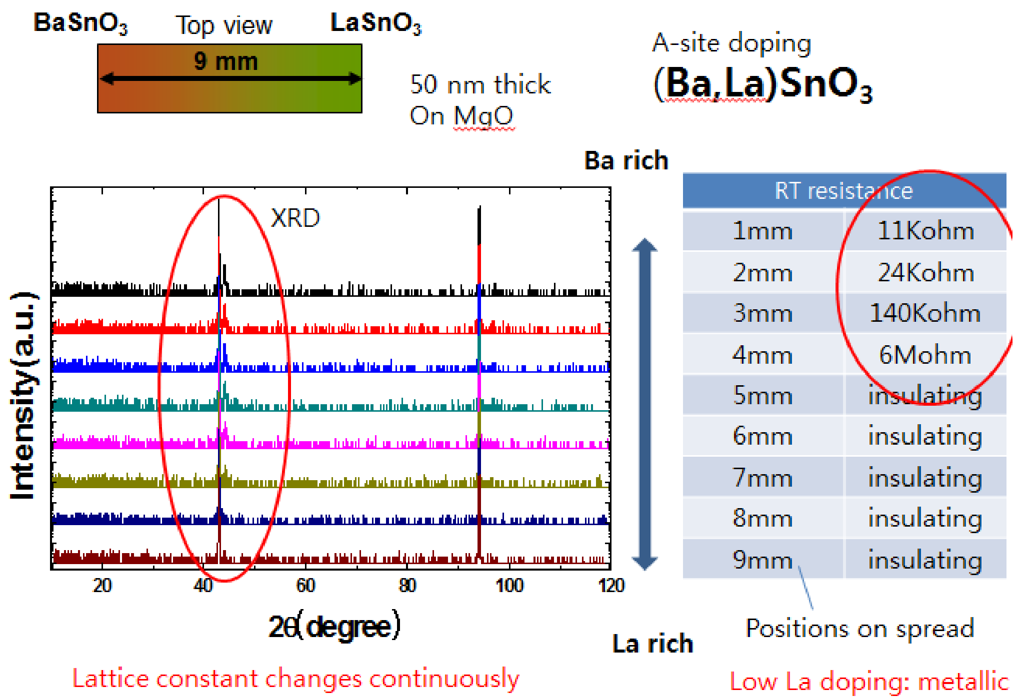

Fig. 1 summary of (Ba,La)SnO3 spread

We have found that low La doping gives rise to good conductivity. The table on the bottom right shows the resistance at different positions on the spread at room temperature. This result is consistent with previous bulk studies on this compound. Other spreads we have studied include Ba(Sn,Sb)O3, Ba(Bi,Sb)O3. We note that when we fabricated a Ba(Pb,Bi)O3 composition spread, superconductovity was observed at the correct composition range indicating that the overall method of our technique is sound.

Using the highest conductivity composition (6% La doped BaSnO3), we have fabricated a ionic liquid gating device to further modulate the carrier density using a 33 nm thick film. Figure 2 shows the result of this experiment.

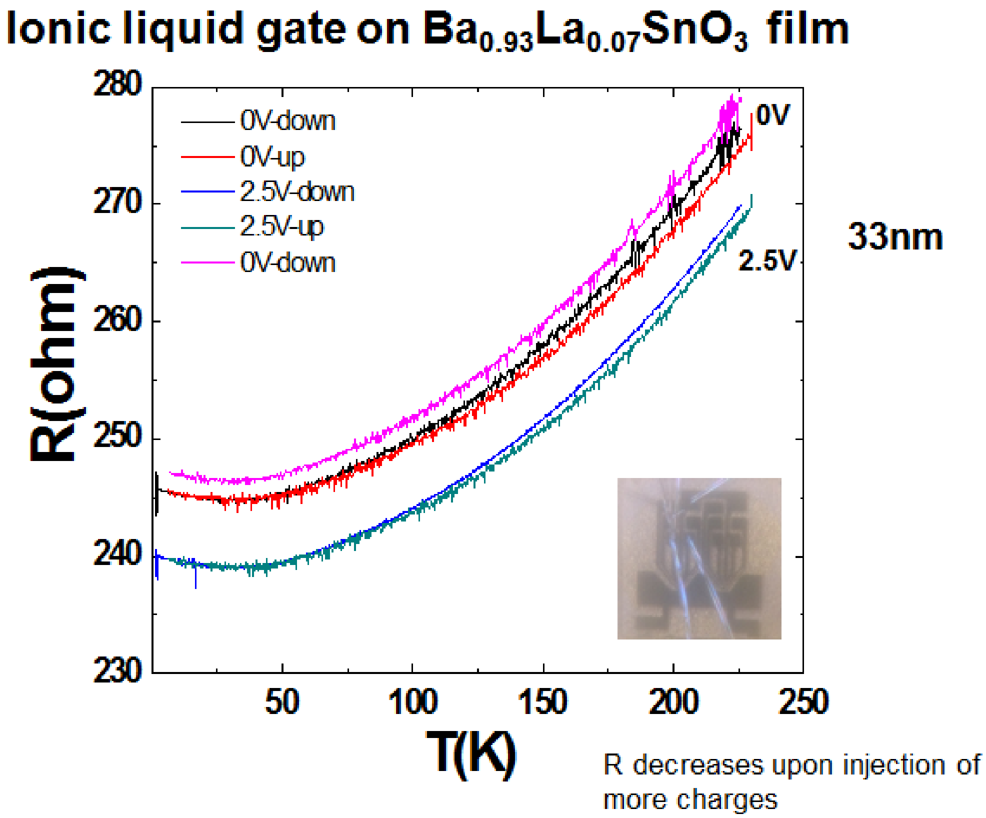

Figure 2. Result of gating into (Ba,La)SnO3 using ionic liquid

The result shows that indeed the resistance can be lowered by applying a gate voltage to the device and cooling down indicating that carriers can be injected. So far no indication of superconductivity has been observed down to 4.2 K.

Invited presentations (with some content supported by MURI**)**

<u>Paul Canfield:</u>

"Why did you do what you did, why did you get what you got?" Physics Seminar, Max Plank Institute, Dresden, June 27, 2013.

"Why did you do what you did, why did you get what you got?" Physics Seminar, Karlsruhe Institute of Technology, Karlsruhe, July 1, 2013.

"The Grass is Always Greener…Things I have learned from Superconductors that Rick was not looking at." Invited Talk, Superconductivity at 300 mK and Beyond Workshop, University of Maryland, November 23-24, 2013.

"Cooking, Fishing, and Jogging Through Phase Space: A Practical Guide to Discovering and Understanding New Materials," Rice University, Physics Colloquium, April 9, 2014.

"Fe-based Superconductors: What we hope we have learned and where we hope we are going" Plenary talk, ICSM 2014, Antalya, Turkey, April 28, 2014.

"Cooking, Fishing, and Jogging Through Phase Space: A Practical Guide to Discovering and Understanding New Materials," UC Irvine, Physics Colloquium, May 15, 2014.

“Design and Growth of Novel Materials”, Two hours Summer School lecture at Brockhouse Institute for Materials, McMaster University, Canada, May 28, 2014.

“Is “(Towards) Room Temperature Superconductivity” even the right direction?” 90 minute invited talk / discussion, Lorentz Center Workshop, Leiden, Netherlands, July 1, 2014

“Solution growth as a test of phase diagrams”, Invited talk at CMI Thermo-workshop, September 10, 2014.

M. B. Maple and his group:

“Superconductivity of electron-doped $LnOBiS_2$ (Ln = lanthanide) compounds at ambient and high pressure,” Superconductivity at 300 mK and Beyond Workshop, University of Maryland, College Park, MD, November 23-24, 2013.

“Novel d- and f-Electron Materials Under Extreme Conditions of Pressure, Temperature, and Magnetic Field,” 2014 Stewardship Science Academic Programs (SSAP) Symposium, North Bethesda, MD, February19-20, 2014.

“Materials Trends in Different Classes of Superconductors: From Heavy Fermion Compounds to Iron Pnictides and Beyond,” 4th International Conference on Superconductivity and Magnetism (ICSM2014), Antalya, Turkey, April 27-May 2, 2014. (Plenary lecture)

*Duygu Yazici “Superconductivity in BiS_2-based compounds,” March Meeting of the American Physical Society, Denver, CO, USA, March 2014.

Johnpierre Paglione and his group:

J. Paglione, “Topological Insulators and Superconductors”, 59th Annual Magnetism & Magnetic Materials Conference, Honolulu, HI, November 2014.

S.R. Saha, “Separation of antiferromagnetism and high-temperature superconductivity in Ca1-xLaxFe2As2”, Int. Workshop on Physics and Chemistry of Novel Superconductors, Okayama, Japan, Nov. 2014.

J. Paglione, “Separation of antiferromagnetism and high-temperature superconductivity in Ca1-xLaxFe2As2”, 2nd International Conf. on Multi-Condensate Superconductors and Superfluids, Italy, June 2014.

J. Paglione, “Separation of antiferromagnetism and high-temperature superconductivity in Ca1-xLaxFe2As2”, 13th International Ceramics Conference- 6th Forum on New Materials, Italy, June 2014.

Richard L. Greene:

R. L. Greene, “Recent results from the UMD-ISU-UCSD MURI project on search for new and practical superconductors”, Superconductivity Program Review, Arlington, VA. 18 August 2014.

Ichiro Takeuchi:

Data driven approaches to combinatorial discovery, Euromat, Seville, Spain, September 11th, 2013.

Integrated materials discovery engine, MRS Fall Meeting, Dec 2nd, 2013.

Integrated materials discovery engine, European MRS, Lille, France, May 27th, 2014.

Invited seminar: Combinatorial materials synthesis, practical materials informatics, and the Materials Genome Initiative, National Institute for Materials Science, Tsukuba, Japan, July 16,17